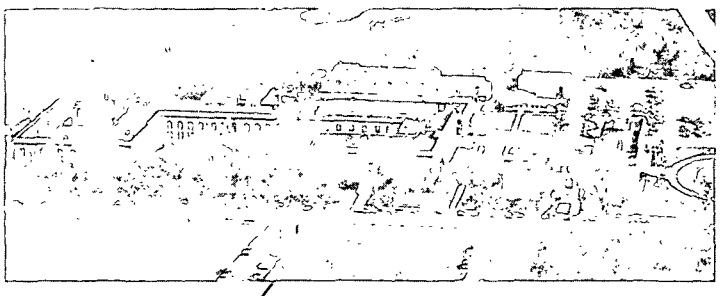

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CHLORINE DIOXIDE MODIFICATION OF SOFTWOOD LIGNIN

N. G. VANDER LINDEN AND G. A. NICHOLLS

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White spruce lignin can be significantly modified by chlorine dioxide while remaining in wood in a water insoluble form. It is no longer fully accounted for by lignin analyses and while some of the lignin monomer units have survived with no significant structural change there have been substantial changes in other units. These changes include loss of methoxyl and the formation of about 1.5 carboxyl substituents per degraded lignin monomer unit. Additional changes include: (a) the elimination of ring conjugated double bonds and/or carbonyls, (b) chlorination in the 6-position of a few aromatic rings capable of yielding 6-chlorovanillin on oxidation with cupric oxide, and (c) formation of easily hydrolyzable chlorine substituents, possibly including chloro-carboxylic acids and chloro-α,β-unsaturated carbonyl structures present in chromophores that are harder to reduce than the naturally occurring chromophores.

Knowledge on structural changes in the modified lignin was obtained with the help of various spectroscopic measurements and provides a better basic understanding of why chlorine dioxide-modified lignin is partially soluble in alkali, as in chlorine dioxide-alkali pulping studies reported previously.

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CHLORINE DIOXIDE MODIFICATION OF SOFTWOOD LIGNIN

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After reaction of white spruce groundwood with chlorine dioxide, at yields in excess of 97%, lignin *in situ* is no longer completely discernible by Klason plus acid-soluble lignin analyses, and has lost aromatic methoxyl without an equivalent loss of lignin material. For reaction with 6% chlorine dioxide, lignin *in situ* contains about 0.9% chlorine, part of which is attached to aromatic rings at the six position, as shown by cupric oxide degradation to 6-chlorovanillin, and 75% of which hydrolyzes to chloride ion, typical of possible chlorine-substituted lignin degradation products. Surviving *in situ* lignin monomer units (including alkylaryl ethers), which are the precursors of aromatic degradation products from cupric oxide reaction, have no significant structural changes. Infrared spectra indicate that 20-25% of the original aromatic structures are degraded; carboxylic acids are formed, some of which apparently have α-chloro substituents and from analyses there are about 1.5 carboxyl substituents per degraded lignin monomer unit; there is evidence for the possible presence of lactones. Infrared spectra, including difference spectra for unreduced, uranium(III) and dithionite reduced groundwood before and after reaction with 6% chlorine dioxide indicate: the occurrence, in all samples before reduction, of α,β-unsaturated carbonyls mainly in structures other than quinones, and after chlorine dioxide reaction, the possible occurrence of chloro-α,β-unsaturated carbonyl structures as well as the elimination of ring conjugated double bonds and/or carbonyls. Ultraviolet and visible spectra on the same materials support not only these indications, but also a decrease in aromatic structures, and the formation of new chromophores, possibly including chloro-α,β-unsaturated carbonyl structures.

INTRODUCTION

In oxidative delignification by chlorine dioxide-alkali to produce high-yield pulps from hardwoods[1] and softwoods[2] the oxidant's reaction with lignin is mainly on the basis of modifying its structure enough so that, although it doesn't become water soluble, it is removable by aqueous alkali[3]. Studies on the reaction of chlorine dioxide especially with lignin model compounds indicate oxidative ring opening and quinone formation occur during lignin degradation, but the amount known about the changes in chemical structure of lignin remaining *in situ* is relatively limited[4] and the aim of this research is to learn more. For this purpose white spruce (*Picea glauca*) sapwood chips were processed into refiner groundwood, Wiley milled, then extracted with alcohol-benzene and hot water, as detailed in the experimental part and elsewhere[5].

RESULTS AND DISCUSSION

Reaction to completion of extracted, white spruce groundwood with up to 9% chlorine free, chlorine dioxide gave uniform pink, pale orange and light yellow products in down to about 97% yield as in Figure 1. This shows the relative amount of acid-soluble lignin in the reacted groundwood increases as oxidant is consumed, as also has been observed by others[6-8], so that the Klason acid insoluble method becomes progressively less suitable for lignin estimation. Also, as oxidant is consumed, the sum of Klason lignin plus acid-soluble lignin is increasingly less than the calculated minimum amount of lignin present in the products, as based on total lignin in the groundwood minus yield loss. Hence the lignin *in situ* is no longer completely discernible by Klason plus acid-soluble lignin analyses and considerable chemical modification is indicated.

Data from methoxyl and chlorine analyses are presented in Table I. From model compound studies[4] it is possible that some of the remaining methoxyl is from structures such as methyl esters of muconic acids derived from lignin degradation, in which case, on the basis of earlier demethylation studies[10], these structures would be expected to demethylate upon hot distillation. However, only about 2% of the total methoxyl was obtained upon hot distillation (Table I) indicating the relative absence of methyl esters of muconic acids or other readily demethylated structures such as chloro-methoxybenzoquinones[10]. Thus of the original aromatic methoxyl, after reaction with 6% chlorine dioxide, 2.94/4.06 or about 73% is preserved, whereas on a material basis lignin content has apparently decreased from 26 to 22.6% (Figure 1 with correction for Cl content) or only by about 10% at the most, which further points to significant structural modifications to the lignin remaining in the reacted groundwood.

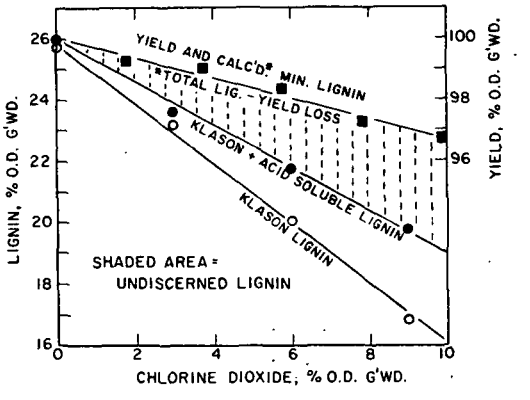

Fig. 1. Yield, Klason lignin, acid soluble lignin[9] and calculated minimum lignin content of products from reaction of extracted *Picea glauca* groundwood with chlorine dioxide (final pH ca. 2).

TABLE I

METHOXYL AND CHLORINE ANALYSES[a]

ClO_2, %	OCH_3, %	Cl, %
0	4.06	0.13
3.0	3.66	0.62
6.0	3.04[b]	0.85
9.0	2.43	1.32

[a] Ovendry extracted groundwood basis.
[b] Methoxyl by hot distillation, 0.07%

LOCATION OF CHLORINE IN MODIFIED LIGNIN

The amount of bound chlorine in the groundwood reacted with 6% chlorine dioxide (Table I) represents about 0.2 Cl substituents per lignin monomer unit which is much less than the 0.75-1.25 Cl substituents found in chlorinated pulp lignin[11]. Since under acidic conditions elemental chlorine is a reaction intermediate in the reduction of chlorine dioxide and lignin undergoes chlorine substitution particularly in the 6-position[11], this could account for part of the bound chlorine.

This was confirmed by alkaline cupric oxide degradation based on an existing method[12], with gas chromatographic separation and mass spectral identification of the major peaks shown in Figure 2 to give results as in Table II. Compound identification included comparisons of retention times and mass spectra with those of known compounds. The yields of vanillin and acetovanillone from the unreacted groundwood are comparable to those obtained previously for white spruce[13] and the formation of vanillic acid is expected from similar oxidations of other softwoods[14]. In addition to obtaining 6-chlorovanillin from the chlorine dioxide-reacted groundwood, on the vanillic acid peak there was a shoulder indicative of 5-chlorovanillin which has a comparable retention time, but the amount was relatively small and no positive identification was made.

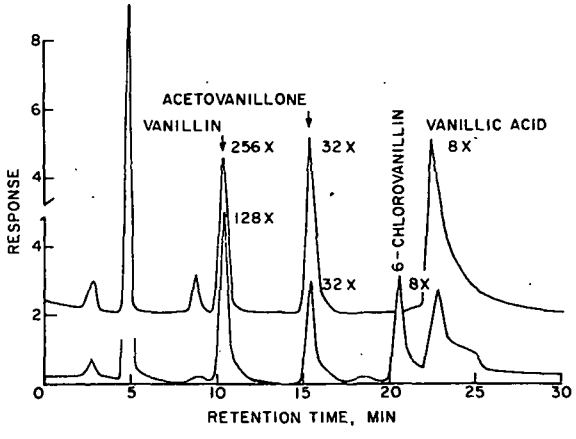

Fig. 2. Gas chromatograms of alkaline cupric oxide reaction products from groundwood (upper curve) and 6% chlorine dioxide-reacted groundwood (lower curve).

TABLE II

YIELDS OF MAJOR PRODUCTS[a] FROM ALKALINE CUPRIC OXIDE DEGRADATION

Product[b]	Groundwood	Groundwood EX-6% ClO_2
Vanillin, %	16.0	9.6
Acetovanillone, %	3.0	2.0
6-Chlorovanillin, %	Nil	0.9
Vanillic acid, %	2.5	1.7

[a] Separation and identification by GC and MS as in experimental part.

[b] Weight percent of equal amounts of lignin degraded (groundwood, 26.4%; 6% ClO_2 reacted groundwood, 24.6%).

The amount of chlorine in the chlorovanillin represents only a part of the total, 75% of which was found as chloride ion in the aqueous phase after cupric oxide degradation. Since 6- and 5-chlorovanillin have been shown to lose very little chlorine[11] under similar reaction conditions, the chloride ion is concluded to probably arise from alkali hydrolysis of various chlorine derivatives produced during lignin degradation. Such hydrolysis of chlorolignin is well recognized[15], and also occurs extensively in chlorine-substituted o-benzoquinones, muconic acids and aliphatic side-chains representing expected chlorine degradation products of lignin. The formation of products in each of these classes has been confirmed in lignin model studies[16-18].

Spectral evidence for some of the chlorine in the reacted groundwood occurring as α-chloro carbonyl compounds is presented below.

SURVIVING AROMATIC LIGNIN MONOMER UNITS

In Table II it is noted that the chlorine dioxide-reacted groundwood gave significant amounts of oxidation products which continued to contain aromatic aldehydes rather than acids. On the basis of model compound studies[19] this indicates the surviving lignin contains free phenolic groups and/or alkylaryl ethers without α-carbonyl groups in the side-chains. However, survival of free phenolic groups seems unlikely since other studies have shown that chlorine dioxide reacts not only rapidly with phenolic groups in model compounds[18] but also with loss of detectable phenolic groups in pine dioxide lignin[20]. It seems more likely that alkylaryl ethers and not free phenolic groups remain in the surviving lignin units, and these on the whole have no significant increase in α-carbonyl groups.

In Table II also note that, except for 6-chlorovanillin, for the same initial quantity of lignin material the major products after chlorine dioxide reaction were the same but the amounts were only 60-70% of those obtained before. This percentage may seem somewhat low because the methoxyl data above indicate preservation of about 73% of the aromatic units, but the yield of vanillin from oxidation of lignin with phenolic groups which have been methylated is known to be relatively less than for unmethylated lignin[21]. Since the relative amounts of the major products are all in the 60-70% range this suggests the surviving lignin units are without significant change in their side-chains because variation in these probably would cause changes in relative yields[19].

Thus it appears that chlorine dioxide extensively degraded some *in situ* lignin monomer units (probably including those with free phenolic groups), without significantly changing those surviving units which are the precursors of aromatic degradation products from cupric oxide. Furthermore, alkylaryl ethers without α-carbonyl groups remain in these precursors.

STRUCTURAL CHANGES IN MODIFIED LIGNIN

Infrared spectra of unreacted and chlorine dioxide-reacted groundwood had observable differences as in Figure 3, particularly in the 1730 and 1510 cm^{-1} regions. From the relative absorbances at 1510 cm^{-1} on a lignin material basis, using either the absorbance maximum at 1820 cm^{-1} or the line through 1850 and 1550 cm^{-1} maxima as the base line[22], about 20-25% of the original aromatic structures have been degraded, which ties in with the methoxyl analyses. Loss of aromatic ring absorption at 1510 cm^{-1} in insoluble lignin after reaction with chlorine dioxide or acidic chlorate is supported by other spectral data[20,23].

The specific nature of changes in Figure 3 is better uncovered, as in Figure 4, by the difference spectrum obtained using comparable amounts (same absorption 2900 cm^{-1}) of unreacted and reacted materials. This figure

shows chlorine dioxide causes gains in absorption in the carbonyl region, particularly at 1710, 1720 and 1760 cm^{-1}, a small gain near 1640 cm^{-1}, possibly due to interference from water, and gains in the C-O stretch region, namely 1180-1200 cm^{-1}. There are also losses in the aromatic region, particularly at 1510 and 1580-1600 cm^{-1}, small losses at 1420-1460 cm^{-1} relatable to demethylation and moderate losses at 1200-1300 cm^{-1} where alkylaryl ethers and phenols absorb[24]. The loss at 1580 cm^{-1} is indicative of degradation of aromatic structures with external conjugation[25].

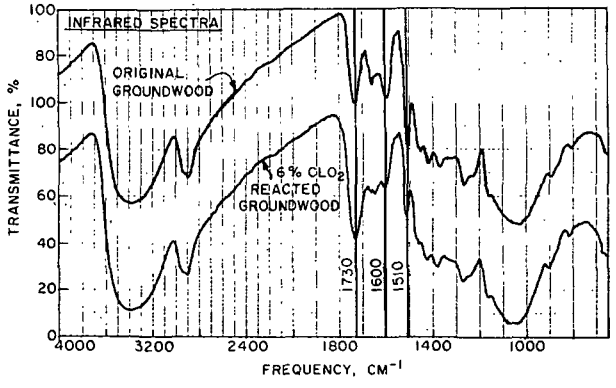

Fig. 3. Infrared spectra of extracted Picea glauca groundwood before and after reaction with 6% chlorine dioxide.

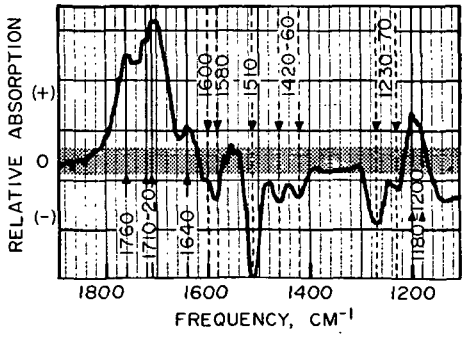

Fig. 4. Infrared difference spectrum showing gains and losses of absorption upon reaction of extracted Picea glauca groundwood with 6% chlorine dioxide.

To further elucidate the above, unreacted and reacted groundwood were carefully neutralized to pH 9.2 with sodium hydroxide following which equal weights of materials before and after neutralization had no difference in absorption at 1510 cm^{-1}. The spectra also showed that neutralization resulted in much of the carbonyl region gain, upon reaction with chlorine dioxide, being shifted to the 1600 cm^{-1} carboxylate ion region. As evident from the upper difference spectrum in Figure 5 for reacted groundwood before and after neutralization, this shift arose from losses of carboxyl carbonyl absorption at 1720-40 cm^{-1} and broad band gains at 1560-1620 cm^{-1} in the anti-symmetric stretching region for carboxylate and α-chlorocarboxylate ions[26]. The reason for the lack of gain in the 1350-1450 cm^{-1} region for symmetric stretching of carboxylate ions[26] is unclear. It may be due to a compensating loss of absorption and/or to other factors, including possibly the base-line method used[22] being unsuited to this case. The losses around 1180-1230 cm^{-1} probably reflect changes in the C-O bonds of carboxylic acid groups upon ionization.

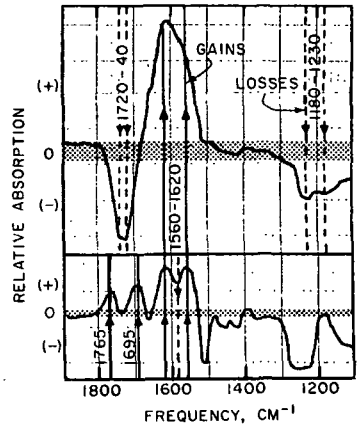

Fig. 5. Infrared difference spectra showing gains and losses of absorption (a) upon neutralization after reaction of groundwood with chlorine dioxide (upper curve) and (b) on a sodium salt basis, of groundwood before and after reaction with chlorine dioxide (lower curve).

By potentiometric titration the 6% chlorine dioxide-reacted groundwood contained 1.9% carboxyl, after correction for a relatively minor amount in the unreacted extracted groundwood[5]. Assuming, for convenience, a value of 200 as the molecular weight of lignin and degraded lignin monomer units, this means there is an average of about 1.5 carboxyl substituents per degraded monomer unit. The possibility that some of these carboxyls apparently have α-chloro substituents is consistent not only with chloride ion formation, as found from cupric oxide degradation, but also with spectroscopic evidence as above and below.

The lower difference spectrum in Figure 5 for neutralized groundwood before and after reaction with 6% chlorine dioxide, shows reaction resulted in carbonyl region gains at 1765 and 1695 cm^{-1}. The former is at about the frequency noted for γ-lactone acids[27] isolated after reaction of lignin model compounds with peroxyacetic acid. The possible presence of a lactone structure is further reinforced by the confirmed formation of such compounds from chlorine dioxide oxidation of phenols related to lignin[20,27]. The gain at 1695 cm^{-1} compares with an absorption gain at 1700 cm^{-1}, obtained when α-lignosulfonic acid is chlorinated and related to carbonyl absorption when chlorine is introduced into aldehydes, ketones and o-quinones[28]. Further support for the gain at 1695 cm^{-1} in lower Figure 5 possibly arising from chloro-carbonyl groups is discussed later.

In the lower curve of Figure 5 gains are also seen which are compatible with corresponding gains at 1560-1620 cm^{-1} in the upper curve, while losses in the aromatic region possibly at 1580 cm^{-1}, at 1510 cm^{-1} and down to 1200 cm^{-1} correspond to similar losses already discussed for Figure 4.

Thus infrared spectra indicate that, after chlorine dioxide reaction, (a) from loss of aromatic absorption about 20-25% of the in situ lignin monomer units have been degraded, which is supported by methoxyl data, and there is evidence for loss of external conjugation; (b) out of an average of about 1.5 carboxyl substituents per degraded in situ lignin monomer unit, a significant portion possibly is α-chloro carboxylic acid, which is supported by chloride ion formation in the cupric oxide degradation; (c) from gains, other than from carboxyl, in the carbonyl absorption region lactone structures and α-chloro carbonyl compounds are possibly present in the degraded in situ lignin.

CHROMOPHORES IN MODIFIED LIGNIN

Note that upon reaction of the groundwood with chlorine dioxide most of the absorption increase in the carbonyl region is at about 1680-1780 cm^{-1} (Figure 4) and is due to increase in carboxyl groups and possibly some lactones (Figure 5) without there being marked change around 1660 cm^{-1} attributable to structures such as unchlorinated quinones or α-carbonyl aromatic compounds[29]. Nevertheless, increases in color observed after reaction with chlorine dioxide, an expectation from model compound studies that quinones might be formed[10,20,30], and indications of the possible formation of chloro-carbonyl groups (Figure 5) led to consideration of chromophore structures in the modified lignin.

From infrared difference spectra for unreduced and reduced white spruce groundwood it was shown, as in upper Figure 6, that reductions by uranium (III) salt and sodium dithionite resulted in absorption losses at 1660 and 1600 cm^{-1}. On an approximate quantitative basis the dithionite was about 65% as effective as uranium (III) at 1660 cm^{-1}. This indicates the presence of α,β-unsaturated conjugated carbonyls, such as in quinones, and α-carbonyl aromatic compounds, and that about 35% or one-third are of the latter type[29].

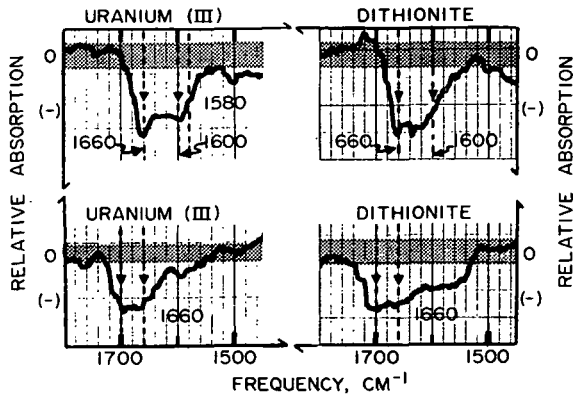

Fig. 6. Infrared difference spectra showing losses of absorption upon reduction of groundwood (upper curves) and groundwood after reaction with chlorine dioxide (lower curves), with uranium (III) salt (U^{+3}) and sodium dithionite (DT), using 6 e. equiv. of reductant.

After reaction with chlorine dioxide, difference spectra for unreduced and reduced materials, as in lower Figure 6, continued to show losses in the 1660 cm^{-1} region reflecting the reduction of α,β-unsaturated carbonyls as in quinones, flavones, etc.[29]. However, since quinones reduce to benzene rings with an increase in absorption at about 1510 cm^{-1} where no significant change is observed in Figure 6, apparently only a small fraction of the α,β-unsaturated carbonyls occurs as quinones. In lower Figure 6 new losses upon reduction appear particularly around 1700 cm^{-1} and, certainly in the case of dithionite, the losses extend over a broad band of frequencies down to 1550 cm^{-1}. The losses around 1700 cm^{-1} correspond to a gain, upon chlorine dioxide reaction, at about the same frequency (lower Figure 5) and this possibly arises from the formation of chloro-carbonyl groups, as noted above. Conceivably, this absorption loss is from reduction of α,β-unsaturated carbonyls which have been chlorinated since these would be expected to absorb at frequencies progressively higher than 1660 cm^{-1} upon progressive halogenation[31].

Difference spectra for unreduced and uranium (III) reduced materials from before and after chlorine dioxide reaction (left curves in Figure 6) show the latter caused disappearance of the loss in absorption at 1580-1600 cm^{-1}. This means chlorine dioxide eliminated reducible groups absorbing at 1580-1600 cm^{-1} or, that is, ring conjugated double bonds and/or carbonyls, which are reduced by uranium (III) but not substantially by dithionite[29], and which cause a lowering of aromatic ring absorption intensity in this region when reduced[25]. The similar loss at 1580 cm^{-1} noted in Figure 4 reinforces this finding.

Ultraviolet and visible absorption spectra of groundwood as in the above, were obtained from compacts using a modification[5] of a previously described method[32]. Spectra of the unreacted groundwood, the 2% and 6% chlorine dioxide-reacted groundwood given in Figure 7 have ultraviolet absorption curves with maxima at 280 nm, typical of the aromatic ring structure of lignin, and with shoulders around 350 nm, typical of carbonyl groups and unsaturated carbon-carbon double bonds conjugated with an aromatic ring[33]. However, there is a progressive decrease in absorption at 280 and 350 nm, with increase in chlorine dioxide reaction, in accord with the decrease in aromatic structures and ring conjugated carbonyls and/or double bonds, as discussed above. In the visible region the chlorine dioxide-reacted materials have significantly more absorption than the groundwood, with the 2% chlorine dioxide-reacted material absorbing most strongly from 450-570 cm^{-1}.

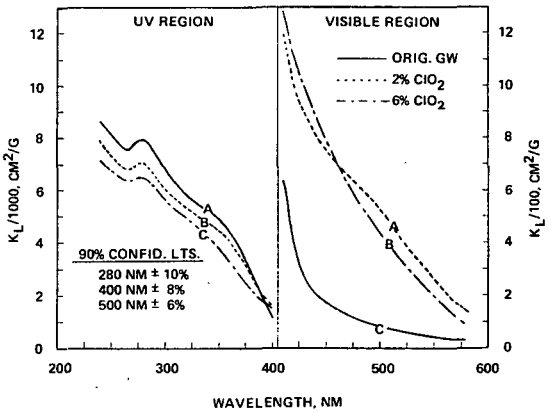

Fig. 7. Absorption spectra of extracted white spruce groundwood (curve A), groundwood reacted with 2% chlorine dioxide (curve B) and groundwood reacted with 6% chlorine dioxide (curve C).

Reduction of groundwood and chlorine dioxide-reacted groundwoods with 6 e. equiv. of uranium (III) and dithionite resulted in considerable lowering of absorption, especially around 350 nm for groundwood and 2% chlorine dioxide-reacted groundwood as expected on the basis of the above. For the 2% and 6% chlorine dioxide-reacted groundwoods, although there were similar large reductions in absorption in the visible region, significant absorption remained, as illustrated in Figure 8 for the 6% chlorine dioxide-reacted groundwood. Unlike the unreacted groundwood for which uranium (III) more effectively removed chromophores, as it does in other softwoods[29], the chromophores in chlorine dioxide-reacted groundwood were less effectively removed in the visible region by uranium (III) than by dithionite. Presumably this is due to the formation of new chromophores, possibly including chloro-α,β-unsaturated carbonyl structures such as show infrared absorption around 1700 cm^{-1}. In view of the known deleterious effect of heavy metal ions on brightness[34] a check was made for the presence of heavy metal ions by spectrographic analysis but no significant concentrations were detected.

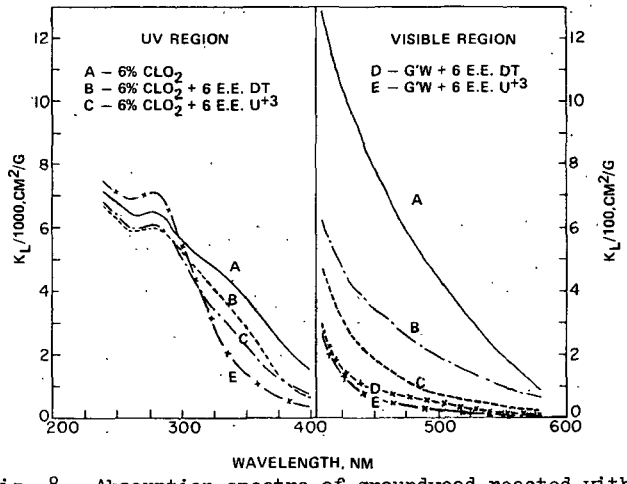

Fig. 8. Absorption spectra of groundwood reacted with 6% chlorine dioxide (curve A), then subsequently reduced with uranium (III) (curve B) and dithionite (curve C), and partial spectra of groundwood reduced with uranium (curve D) and dithionite (curve D).

EXPERIMENTAL

MATERIAL PREPARATION

Two 4-ft bolts with 3-6 inch diameter were cut from two 20-yr-old Appleton grown white spruce (Picea glauca), debarked, deknotted, the sapwood chipped and the chips converted to refiner groundwood. This was air dried at ambient temperature, Wiley milled using a No. 5 screen, extracted with alcohol-benzene essentially as in TAPPI T 6 m-59, air dried, extracted with hot water (80°C for 5 hr) then filtered, washed, air dried, and stored in the dark at ambient temperature.

GROUNDWOOD AND CHLORINE DIOXIDE REACTION

Forty-gram batches of extracted groundwood were reacted at 3% consistency and 35°C with 3-9% chlorine free, unbuffered chlorine dioxide in 2-liter bottles after being in contact with distilled water overnight to ensure uniform wetting. As the reaction neared completion after 2-8 hr, potassium iodide-starch test paper was used to determine the end point, then the contents were filtered on a Buchner funnel, washed including by diffusion overnight, air dried at ambient temperature, yield determined, and stored in the dark.

ANALYTICAL PROCEDURES

(1) Lignin content: Klason lignin was based on TAPPI 222 os-74 and acid-soluble lignin determination was based on the method of Pearl and Busche[9].

(2) Methoxyl: Total and easily hydrolyzable methoxyl were based on TAPPI T 209 su-72, and the method of Dence, et al.[10], respectively.

(3) Carboxyl: A suspension of groundwood (2 g o.d. in 50 ml water) was titrated with 0.2N NaOH while plotting pH vs. ml of base to determine the end point from the maximum slope, and the result further confirmed by the calcium acetate method of Meesook and Purves[35], except that hydrogen ion liberated by calcium ion exchange was determined potentiometrically.

(4) Organic chlorine: Determined via combustion in a Schöniger flask followed by Volhard titration of the liberated chloride.

(5) Inorganic elements: Determined by standard spectrometric techniques using a modified Bausch & Lomb Spectrograph (1-1/2 meter grating).

CUPRIC OXIDE DEGRADATION

Unreacted and chlorine dioxide-reacted groundwoods were degraded in alkaline cupric oxide using a modification of the Pearl and Beyer procedure[12]. The sample containing ca. 3.7 g of lignin was reacted with hydrated cupric oxide (26.5 g) and 160 ml of 2N NaOH for 3 hr at 170°C in a stainless-steel bomb after which the contents were filtered, washed with 2% aqueous sodium hydroxide then with ether and the combined filtrate plus washings acidified with sulfuric acid to pH 2 prior to continuous extraction with ether.

GAS CHROMATOGRAPHY AND MASS SPECTROSCOPY

Gas chromatographic analyses used a Varian Model 1520 chromatograph with a 10% S.E. 30 on Chromosorb G, AW, DMCS, 1/4 in. x 6 ft S.S. column at 165°C, injecting acetone solutions of the ether solubles from the cupric oxide degradation studies and various chromatographically pure knowns, and with p-dibromobenzene as internal standard. Tentative identification of the chromatographic peaks from relative retention times was confirmed by mass spectroscopy using a Du Pont Instruments Model 21-491 spectrometer interfaced via a jet separator with a Varian Model 1440-1 gas chromatograph (flame ionization). Gas chromatographic and beam monitor responses were shown by a Hewlett-Packard Model 7128A recorder and mass spectra by a Century GPO 460 recorder.

SPECTROSCOPIC MEASUREMENTS

Infrared spectra were obtained by transmittance measurements using BDH infrared grade KCl pellets containing Wiley milled (80 mesh) samples that were pulverized in a stainless-steel capsule for six periods of 5 min on a mixer-mill with cooling between each period. Drying was for 24 hr in a vacuum oven at 40°C, and about 2.2 mg of material was thoroughly mixed with potassium chloride (250 mg) for pellet making in a conventional press allowing 6 min under vacuum and 10 min at 10 tons force. For difference spectra, pellets containing equivalent amounts (same absorption at 2900 cm^{-1}) of the two materials of interest were placed in the reference and sample beams. For preliminary spectra and more detailed studies Perkin-Elmer Model No. 700 and 621 infrared spectrophotometers were used, respectively.

Ultraviolet and visible absorption spectra were obtained using a modification[5] of a previously described method[32] and a Beckman Model DK-2 spectrophotometer equipped with an integrating sphere to provide transmittance and reflectance measurements on sheets of Whatman No. 40 filter paper, reflectance measurements on compacts of Wiley milled (80 mesh) Whatman No. 40 paper, and reflectance measurements on compacts of Wiley milled (80 mesh) groundwood materials diluted to about a 1% lignin concentration with the milled Whatman No. 40 paper. The compacts were made in a 3.5-cm diameter die with the compact face pressed against a silvered plate 20 min at 1 ton total force. Reflectance measurements were made at four different positions on the face of the compacts using a magnesium oxide compact for reference.

SODIUM DITHIONITE AND URANIUM (III) REDUCTIONS

Unreacted and chlorine dioxide-reacted groundwoods were reduced with 6 electron equivalents of sodium dithionite (DT) and uranium (III) using the methods of Polcin and Rapson[29]. The DT reaction was followed by a 5-min

soak in 0.1N hydrochloric acid before final washing and air drying and the U^{+3} reaction included washing with 0.05M disodium dihydrogen ethylenediaminetetraacetate dihydrate (EDTA), then suspending the washed sample in 0.1N hydrochloric acid for 5 min before final washing and air drying.

ACKNOWLEDGMENTS

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